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14. ABSTRACT Damping enhancement can lead to significant enhancement of mission capability in Army structures such as those used in rotorcraft, for instance. The objective of this investigation is to explore and understand the fundamental mechanisms of damping provided by carbon nanotubes (CNTs) in polymer-based materials such as those used to fabricate fiber composites, and to use this new understanding to explore further enhancements in damping. In addition, the feasibility of using carbon nanotubes for damage detection in polymeric composites is explored.					
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## Report Title

Structural Damping and Health Monitoring Enhancement via Multifunctional Carbon Nanotube-Based Composites Tailoring

### ABSTRACT

Damping enhancement can lead to significant enhancement of mission capability in Army structures such as those used in rotorcraft, for instance. The objective of this investigation is to explore and understand the fundamental mechanisms of damping provided by carbon nanotubes (CNTs) in polymer-based materials such as those used to fabricate fiber composites, and to use this new understanding to explore further enhancements in damping. In addition, the feasibility of using carbon nanotubes for damage detection in polymeric composites is explored. Multi-scale micromechanics - molecular dynamics models of CNTs embedded in polymer resin have been developed to simulate damping of aligned and unaligned CNTs. The models point to the importance of CNT morphology and functionalization in tuning overall damping behavior. Novel methods of aligning and chaining carbon nanofibers and CNTs with AC electric fields have been developed and used to make epoxy-based nanocomposites. Multiphysics models of CNT chain formation in liquid epoxy explain the experimental observations of a peak growth rate at an optimal electrical frequency. A model of a polymer composite containing CNTs indicated that a crack could be detected with significantly greater sensitivity if external tuned resonance circuitry is used.

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**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

#### (a) Papers published in peer-reviewed journals (N/A for none)

Liu, A., Wang, K. W., and Bakis, C. E., "Multiscale Damping Model for Polymeric Composites Containing Carbon Nanotube Ropes," J. Composite Materials, 44(19): 2301-2323 (2010). <http://dx.doi.org/10.1177/0021998310365176>.

**Number of Papers published in peer-reviewed journals:** 1.00

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#### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

**Number of Papers published in non peer-reviewed journals:** 0.00

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#### (c) Presentations

**Number of Presentations:** 0.00

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#### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Liu, A., Wang, K. W., and Bakis, C. E., "Damage Detection of Epoxy Polymer via Carbon Nanotube Fillers and External Circuitry," World J. Engineering, Vol. 7, Supplement 2, Sept. 2010, Proc. Intl. Conf. on Composites/Nano Engineering, ICCE-18, paper 358, 2 p.

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):** 1

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#### Peer-Reviewed Conference Proceeding publications (other than abstracts):

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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#### (d) Manuscripts

Liu, A, Wang, K. W., and Bakis, C. E. "Effect of Functionalization of Single-Wall Carbon Nanotubes (SWNTs) on the Damping Characteristics of SWNT-Based Epoxy Composites via Multiscale Analysis," Composites A. Submitted 25 Aug 2010. In review.

**Number of Manuscripts:** 0.00

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#### Patents Submitted

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## Patents Awarded

### Awards

K.W. Wang

-Fellow of the Institute of Physics (IOP), 2010

-Associate Fellow of the American Institute of Aeronautics and Astronautics, 2010

### Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ambuj Sharma	0.05
<b>FTE Equivalent:</b>	<b>0.05</b>
<b>Total Number:</b>	<b>1</b>

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ailin Liu	0.50
<b>FTE Equivalent:</b>	<b>0.50</b>
<b>Total Number:</b>	<b>1</b>

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Kon-Well Wang	0.07	No
Charles E. Bakis	0.07	No
<b>FTE Equivalent:</b>	<b>0.14</b>	
<b>Total Number:</b>	<b>2</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): .....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....	0.00

**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PHDs**

<u>NAME</u>
<b>Total Number:</b>

**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

Multiscale micromechanics / molecular dynamics models of CNTs embedded in polymer resin have been developed to simulate damping of aligned and unaligned CNTs. The models point to the importance of CNT morphology and functionalization in overall damping behavior of the composite. With ~1% carbon atoms in the CNT covalently bonded to the epoxy resin, the interfacial shear strength increases by 25 times. With functionalization, the onset and completion of the interfacial slip (damping) occurs at higher stress range. CNT functionalization can either enhance or reduce damping of the composite -- depending on the interfacial shear strength and the operational stress range of the chosen matrix material. Aligning CNTs in the loading direction increases damping by ~2x. With different CNT aspect ratios, CNT functionalization can either enhance or reduce loss factor in a predefined operational stress range. Novel methods of aligning and chaining carbon nanofibers and CNTs with AC electric fields have been developed and used to make epoxy-based composites. Multiphysics models of CNT chain formation in liquid epoxy explain the experimental observations of peak chain growth at a certain optimal electrical frequency. It was discovered that, at the high volume fractions of conductive CNTs needed for beneficial damping effects, polarization and alignment of the CNTs is facilitated by reducing the CNT conductivity. This is most effectively done by coating the CNTs with a non-covalently bonded functionalizing agent that not only aids dispersion and bonding with the polymer matrix but also facilitates CNT alignment that benefits damping as well as anisotropic resistivity tailoring for structural health monitoring. A model of a polymer composite containing CNTs indicated that a crack could be detected with significantly greater sensitivity if external tuned-resonance circuitry is used. In particular, the circuitry resonance effect amplifies the magnitudes of the admittance and the admittance change by 25% at the resonance frequency. Furthermore, damage location can be determined.

### **Technology Transfer**

## **Final Report**

### **Structural Damping and Health Monitoring Enhancement via Multifunctional Carbon Nanotube-Based Composites Tailoring**

Proposal No. 51004EG  
Grant No. W911NF-07-1-0395

Period of Performance: July 1, 2007 to Dec. 31, 2010

Charles E. Bakis, Department of Engineering Science & Mechanics, Penn State University,  
University Park, PA 16802  
Kon-Well Wang, Department of Mechanical Engineering, University of Michigan,  
Ann Arbor, MI 48109

#### **I. Research Objectives**

The goal of this research is to advance the state of the art of structural damping by utilizing the characteristics of carbon nanotube (CNT) based composites, building upon the current Penn State research experience in vibration damping, damage detection, and carbon nanotube based materials. More specifically, we want to create composites with dispersed and well-aligned CNT fillers to (a) significantly increase the structural damping level, (b) provide effective means to quantify the inter-tube and tube-resin interfacial strengths (a critical factor to characterize damping in such structures), and (c) explore the feasibility of enhancing the system damage detection capability with resistivity monitoring. We aim to investigate the characteristics of these CNT-based composites to obtain good basic understanding, and develop guidelines to best design such multifunctional CNT-based structures for high damping and health monitoring functions.

The unique features that make CNTs ideal fillers for high performance damping composites are their extremely large surface area, large aspect ratio, high stiffness, and low density characteristics. Preliminary studies at Penn State have shown that adding nanotubes to polymeric matrix can achieve a several-fold increase in damping even with less than 1% of CNTs. This fact makes it feasible to utilize nanotubes in realistic large-scale structures. The recent Penn State investigations also identified some major research issues and opportunities to advance the CNT-based structural system for enhanced damping and damage detection capabilities. It was recognized that a major bottleneck in predicting the damping ability of CNT-based composites is that there is no reliable method for identifying the interfacial strength between CNTs and between CNT and resins, a critical variable required to accurately quantify the stick-slip threshold and load transfer characteristics at these interfaces. It was also recognized that a great improvement of loss factor in designed directions could be achieved by fully dispersing well-aligned CNTs or nanoropes in the polymeric materials. This finding indicates that to further significantly enhance CNT-composite damping, we need to explore the feasibility of CNT alignment in such composites. It has also been observed that, with well-aligned CNT fillers in polymers, one can increase electrical conductivity in the aligned CNT direction without necessarily connecting the CNTs. Moreover, the resistivity of a host fiber composite structure with aligned CNTs in the matrix would be very sensitive to matrix damage in the selected direction, and thus one can

utilize such electrical networks in structural health monitoring by measuring the resistivity variations. Having the ability to detect subcritical matrix damage using the electrical response of CNT-filled matrices would be a major breakthrough in structural health monitoring methods which, up to now, have mainly targeted microfiber failure in composites.

## **II. Approach**

This research aims to explore new ideas and research directions that will advance the state of the art:

- Develop electrical tailoring techniques to achieve composites with well-aligned carbon nanotube fillers. The innovation in this part of the project concerns the development of novel methods of using AC and DC electrical fields to align nanotubes and to form networks of aligned, connected nanotubes in epoxy resins. By altering the field parameters, it will be possible to tailor the texture and distribution of the nanotubes in epoxy and thereby obtain better control over the mechanical, thermal, and electrical properties of the composite material.
- Develop effective means of quantifying the inter-tube and tube-resin interfacial force transfer mechanisms (a critical factor to model damping in CNT-based composites) and characterizing the overall system damping property by developing (a) a micromechanical-based empirical approach using composites with well-aligned carbon nanotube fillers, and (b) a multi-scale computational method. Combined with experimental measurements on composites, this innovative computational approach will explain the damping mechanism from an atomistic viewpoint.
- Significantly enhance the damping ability of structures by utilizing composites with dispersed and well-aligned carbon nanotube fillers.
- Explore the feasibility of enhancing the damage detection capability of structures by utilizing resistivity monitoring on composites with dispersed and well-aligned carbon nanotubes. To-date, several investigations have demonstrated the use of carbon fiber and nanotubes for detecting damage in polymers and fiber reinforced polymer composites. The innovation in our approach in this exploratory part of the investigation is to apply our unique capability to align carbon nanotubes to tailor the anisotropic electrical conductivity of the epoxy resin so that dramatically improved sensitivity to matrix damage in fiber reinforced epoxy composites can be realized.

## **III. Significance**

Primary applications of this research exist for the Army in stability augmentation, vibration control, and health monitoring of rotorcraft, weapon systems, and military vehicles. This will result in system performance improvement, life extension, cost reduction, and enemy detection prevention. Through discussions with the Weapons and Materials Directorate of the Army Research Laboratory (ARL) at Aberdeen Proving Ground (APG), it is apparent that the present effort will greatly benefit their research on lightweight composite structures for weapons systems. In particular, researchers at ARL/APG are interested in enhancing damping and damage detection capability of fiber-reinforced polymers used in dynamically loaded structures such as gun barrels,

projectiles, and in military vehicle electronic equipment enclosures. Throughout this project, we have maintained close contact with researchers at ARL/APG to exchange information on CNT composites research and Army applications. On the other hand, this research also complements the investigators' other ARO and NRTC supported projects in exploring active-passive constrained layer damping treatment and flexible matrix composites for helicopter rotor flexbeam and driveshaft applications. High damping rotorcraft flexbeams with damage detection capabilities will enhance rotor stability and safety while avoiding ground/air resonances, which may result in damperless rotors. For drivetrain systems, although internal structural damping is not desired for supercritical speed driveshafts (due to whirl instability), it will be helpful for vibration suppression of subcritical speed shafts (which are more commonly used in current helicopters). The present research will greatly benefit the design and maintenance of flexible matrix composite shafting for helicopters, which have been under investigation at Penn State by the PIs since 2001 with funding from a variety of sources including the National Rotorcraft Technology Center and the Vertical Lift Consortium. High performance lumped dampers with self diagnostic functions could also be developed utilizing the new nanotube-polymer material, which may be used as lag dampers for rotors or external dampers for supercritical speed driveshafts in helicopters. The investigation could therefore be of interest to the Army Aviation Applied Technology Directorate (AATD), Army-NASA Ames, Army-NASA LaRC, and Army-NASA Glenn engineers. Essentially, the performance of structural systems subjected to dynamic loads and disturbances could be improved by using the results of this research. The engineering community in general will have better tools to design, control, and diagnose structural systems. The existing techniques will be greatly complemented by the findings from this investigation.

#### **IV. Accomplishments**

##### **1. Effect of functionalized CNTs on damping**

The influences of CNT functionalization on interfacial shear strength and hence on damping characteristics of CNT-based composites are explored with a multiscale damping model. The sequential multiscale approach consists of two parts. First, the interfacial shear strength between the functionalized nanotube and the polymer is calculated by simulating a CNT pull-out test using the molecular dynamics method. Interfacial shear strength values obtained from atomic simulation are then applied to a micromechanical damping model of a representative unit cell of a CNT/polymer composite. Using this model, epoxy resin containing well dispersed, aligned or randomly oriented functionalized SWNT ropes are investigated. The molecular dynamics analysis indicates that the interfacial shear strength between the SWNT and the epoxy resin is dependent on different quantities of functional groups on the CNT. As shown in Figure 1, with about 1% carbon atoms in the CNT covalently bonded to the epoxy resin, the interfacial shear strength is about 25 times the value for non-functionalized CNTs in epoxy.



The effective loss factor for the epoxy resin with functionalized CNTs are investigated and compared with the epoxy resin containing non-functionalized CNTs, as shown in Figure 2. With functionalized CNTs, the onset and completion of the interfacial slip occurs at higher cyclic (tension-compression) stress amplitude, although the maximum loss factor does not change. Functionalization can either enhance or reduce damping based on the interfacial shear strength and the operational stress range of the chosen matrix material. Qualitatively speaking, for the randomly oriented case examined in this investigation, the functionalization of CNTs reduces the effective loss factor if the operational stress range is low. However, the functionalization can enhance damping if the operational stress range is high.

The damping behavior of composites with  $0^\circ$  aligned non-functionalized and functionalized nanoropes is shown in Figure 3. It is seen that  $0^\circ$  nanorope alignment improves the composite's damping ability, for composites with either non-functionalized or functionalized CNT ropes, when interfacial slip is a major contributor to energy dissipation (above  $\sim 50$  MPa for both cases).

The nanotube aspect ratio plays a very important role in damping properties, as seen in Figure 4. Both composites with  $0^\circ$  aligned non-functionalized and functionalized nanoropes are plotted and compared in this figure. For both cases, the maximum effective loss factor increases and shifts to higher stress level with the increasing aspect ratio of the carbon nanotubes. The shifting of the loss factor peak indicates that higher stresses are needed to cause the longer nanoropes to slip completely during the cyclic loading.

## **2. Increase damage detection sensitivity with external circuitry**

Being of small size and high aspect ratio, CNTs are promising candidates to detect strain and damage by monitoring electrical resistance in structural fiber reinforced polymer composites. The feasibility of the increase damage detection sensitivity for CNT-composite with external circuitry is explored by a 1-dimensional resistor chain with five components, as shown in Figure 5. A voltage is applied to the entire structure and a circuit element is connected to each component in parallel to detect the damage location. The lumped resistance for each component in the model is calculated with a finite element approach. The representative healthy composite layer and damaged composite layer with a small crack are shown in Figure 6. The finite element analysis indicates a 5.5% decrease of conductivity with one small crack as shown in Figure 6(b).

With the external circuitry, the circuitry resonance effect amplifies both magnitudes of the admittance ( $Y$ ) and the admittance change ( $\Delta Y/Y_0$ ) by 25% at the resonance frequency (Figure 7). With a slightly damaged component IV in the chain, the admittance changes when the external circuitry is in series with the damaged component. Results not show here show that damage has no effect on the output when the circuitry is put on component IV. These observations show that this approach could have potential in identifying the location of the damage as well as the severity.

### **3. Aligning high weight fractions of CNTs in epoxy based composites**

Following the predictions of multi-scale modeling on the effects of CNT volume fraction and CNT aspect ratio on damping, it is desired to manufacture composites with higher weight fractions of long CNTs that are aligned in the direction of loading. Most importantly from the manufacturing standpoint, the CNTs should be well dispersed to achieve the predicted improvement in damping characteristics of the composite. However, the dispersion of CNTs usually results in the reduction of CNT lengths. The shear stresses produced by mechanical agitation cuts the CNTs as the CNTs disperse. Longer the CNTs are exposed to mechanical agitation, the shorter the CNTs get. The as-received CNTs are in agglomerated state. The CNTs are held together tightly in agglomerates by van der Waals forces and mechanical entanglement. To effectively separate CNTs from agglomerates, exposure to mechanical agitation is a must. The use of ultrasonic agitation has been found to most effectively disperse CNTs, but with a serious limitation on preserving the lengths of dispersed CNTs. However, well dispersed CNTs with longer lengths can be obtained by controlling the time of sonication and the viscosity of the solvent medium. By adjusting the viscosity of liquid epoxide and controlling the time of sonication, complete dispersion of multi-walled carbon nanotubes with an average aspect ratio of 60 was achieved in efforts made here at Penn State. Based on the predictions of multi-scale modeling, the dispersed MWCNTs were aligned using AC electric field to maximize damping.

#### **Aligning CNTs in a high weight fraction CNT/epoxy composite**

To effectively align CNTs, individual CNTs must be polarized by the applied electric field. In liquid epoxy suspensions with weight fractions of CNTs more than percolation threshold, the possibility of randomly oriented CNTs forming conducting pathways is high. That is, the conducting pathways pre-exist and are not formed by the applied electric field. On application of electric field to high weight fraction CNT suspensions, the electrons freely flow through the pre-existing conducting pathways. As a result of continuous flow of electrons, the CNTs forming conducting pathways do not polarize. Polarization of an isolated CNT occurs due to the mismatch of conductivity at the interface of CNT and the surrounding medium. Upon the application of an electric field, the conducting electrons in a CNT move in the direction opposite to the field. On reaching the junction between CNT and epoxy, electrons experience resistance to their motion due to the extremely low conductivity of epoxy in comparison to CNTs. As a result, the electrons accumulate at one end of the CNT rendering the other end positively charged. The interaction of electric field with this pair of opposite charges applies a torque to orient CNTs in the field direction. However, if CNTs do not polarize, they cannot align or form chains in the direction of electric field. As can be seen in Figure 8, use of 0.5 wt% unfunctionalized MWCNTs resulted in no difference in DC resistivity between composites manufactured with and without AC electric field. Introduction of electrical anisotropy in a composite is an indicator of preferential alignment of CNTs in the field direction. The DC resistivity decreases in the direction of electric field and increases transverse to the field direction when CNTs align in the field direction. The higher weight fractions of MWCNTs used in this investigation resulted in pre-existing

conducting pathways that prevented the CNTs from polarizing and aligning in the field direction.

To prevent the formation of pre-existing conducting pathways in CNT/epoxy suspension, the conduction between two adjacent CNTs should be reduced. By increasing the resistance between CNTs, free flow of electrons through the conducting pathways can be suppressed to allow individual CNTs to polarize and align in the field direction. The argument of increased polarization of CNTs due to reduced surrounding conductivity can also be understood based on the Maxwell-Wagner polarization model. The polarization of a particle suspended in a medium is related to the conductivities of the particle and

medium by the Claussius-Mossotti (CM) factor given by  $\text{Re} \left[ \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_f}{\tilde{\varepsilon}_f} \right]$ , where

$\tilde{\varepsilon}_p = \varepsilon_p - i \frac{\sigma_p}{\omega}$  and  $\tilde{\varepsilon}_f = \varepsilon_f - i \frac{\sigma_f}{\omega}$  are the complex dielectric constants of particle and

medium respectively,  $\varepsilon$  and  $\sigma$  are the real dielectric constant and conductivity of the particle and the fluid,  $\text{Re}$  stands for the real part of the complex number, and  $\omega$  is the angular frequency of the applied electric field. A higher value of CM factor indicates stronger polarization and more torque on the particles. Figure 9 shows the variation of CM factor with the variation of surrounding medium conductivity. With increasing medium conductivity (which would result due to higher concentration of conducting particles) the value of CM factor decreases, thereby reducing the polarization and torque on the suspended particles. One way to increase the resistance between two CNTs is to coat the CNTs with a thin layer of insulating polymer. Non-covalently functionalized CNTs provide a means for coating the CNTs with a polymer that not only increases the resistance between CNTs, but also facilitates the transfer of load between the CNTs and the matrix.

Non-covalently functionalized MWCNTs were purchased from Zyvex Performance Materials, LLC (Columbus, OH) and were delivered pre-dispersed in Epon 862 at a weight fraction of 2 wt% of the epoxide weight. For studying the effects of non-covalent functionalization on alignment and chaining of MWCNT, composites were manufactured with 0.5 wt% of MWCNTs. The as-received suspension of epoxide/MWCNTs was diluted with appropriate amounts of Epon 862 epoxide to obtain a weight fraction of 0.5% MWCNTs in the composites. AC electric field strength of 100 V/cm at frequencies ranging from 100-100 kHz was used to manufacture the composites. For all the frequencies, the resulting composites with aligned non-covalently functionalized MWCNT had DC resistivities in the field direction less than randomly oriented CNT composites (Figure 10). Relative to the randomly oriented non-covalently functionalized MWCNT material, the transverse DC resistivity of materials prepared with electric fields were greater at lower alignment frequencies (100 Hz to 10 KHz) and slightly less at the highest frequency (100 kHz). The DC resistivity anisotropy ratio, defined as the transverse DC resistivity divided by the parallel DC resistivity, decreased from 650 to 30 on increasing the alignment frequency from 100 Hz to 100 kHz. The decrease in DC resistivity in the field direction and increase in the transverse direction in comparison to random MWCNT composite indicates formation of chains in the field direction. Non-

covalently functionalized MWCNTs were further used to manufacture continuous glass fiber/epoxy composites.

### **Aligning CNTs in continuous glass fiber/epoxy composites**

The weight fraction of non-covalently functionalized MWCNTs used to manufacture glass fiber/epoxy composites was 0.5 wt% of the resin weight. MWCNTs were aligned through the thickness direction of the composites using 1000 V<sub>pk-pk</sub>/cm electric field with sinusoidal variations at 100 and 1 kHz. Alignment of CNTs was investigated in composites with two different fiber volume fractions,  $V_f$ : 45 and 55%. The composites were prepared using the wet-filament winding process. The two orifice sizes used for obtaining 45 and 55 volume percent of fibers were 0.031-in. and 0.038-in., respectively. Figure 11 shows the schematic of experimental set up for aligning CNTs in continuous fiber composites.

The decrease in DC resistivity in the direction of electric field and increase in DC resistivity perpendicular to the electric field are used as indicators of CNT chaining. Figures 12-15 show the effect of applying 100 Hz and 1 kHz electric fields on the DC resistivities of composites with glass fiber volume fractions ( $V_f$ ) of 0.45 and 0.55. The DC resistivities obtained without electric field in the through-thickness direction are also plotted for comparison in these bar charts. The application of electric field reduced the resistivity in the through-thickness direction (direction of electric field) for composites of either glass fiber content, as expected. This reduction was more evident when  $V_f=0.45$  than when  $V_f=0.55$ . This response could be a useful feature for future work on resistance tailoring of composites for improved electrical structural health monitoring.

Surprisingly, the resistivity of the composite in the in-plane transverse direction did not change much compared to the resistivity through the thickness. One would expect the in-plane transverse resistivity to increase because the field was oriented through the thickness. A slightly larger increase in transverse resistivity was seen when using 1 kHz in comparison to 100 Hz. Not much dependence on the  $V_f$  was seen. The increase in in-plane transverse resistivity indicates fewer electrical connections in that direction than in the random case.

The resistivity along the fiber direction is noted to be lower than any other direction when no field is applied during processing. This result suggests that the CNTs are aligned preferentially parallel to the fibers during processing, possibly due to the predominant direction of resin flow parallel to the fibers during compaction prior to cure. Resistivity in the fiber direction increased when using a 100 Hz alignment frequency, but decreased when using a 1 kHz frequency. A possible explanation is that a 100 Hz alignment frequency resulted in CNT chains (oriented in through-thickness direction) spaced farther apart along the fiber direction versus the case of a 1 kHz alignment frequency.

## **V. Technology Transfer**

C. Bakis visited the Army Research Laboratory in Aberdeen, MD in June 2007 at the outset of the project to discuss the pending project with Drs. J. Tzeng and R. Emerson and to present a seminar on recent progress on related research to a group of interested persons at ARL.

Following a visit by a group of researchers from Boeing Helicopter to Penn State in May 2008 to discuss CNT-based composites, a small project was initiated at Penn State to investigate the feasibility of inserting CNTs into prepreg-based composite laminates used in helicopter blades. Initial results show that substantial increases in the interlaminar fracture toughness (nearly a factor of two) can be obtained using the processing method developed in this investigation. The project ran from Dec. 2008 through the end of July 2009. The work was sponsored ultimately by AATD-Ft. Eustis, with Mr. Jon Schuck the point of contact.

Through a related SBIR project for Nextgen Aeronautics and the US Army on the use of nanoreinforcements in rocket motor casings for improved impact resistance, C. Bakis has interacted via telephone conference calls with Keith Roberts and Daniel Carter of the Aviation and Missile Research, Development, and Engineering Center (AMRDEC), Propulsion and Structures Directorate, Aerospace Materials, Redstone Arsenal, AL. C. Bakis is providing expertise to Nextgen on the use of nano-reinforcements in the rocket casing filament winding process to minimize the effect of blunt object impact on burst strength. The current Phase II of this project runs from March 2009 through June 2011. An extension has been awarded for 2011-12. Experience gained in the current ARO project has benefitted this SBIR project.

C. Bakis had discussions with Dr. Dy Le and Dr. Jaret Riddick of the Vehicle Technology Directorate, ARL/Aberdeen, on using networked carbon nanotubes for structural health monitoring in glass fiber composites, based on feasibility studies done in present investigation. This idea led to a follow-on ARO proposal which was funded for year 2010-13.

K. W. Wang has been discussing progress with Dr. Louis Centolanza from AATD.

## **VI. Journal and Conference Papers, 2007-10**

### **Journals**

Sharma, A., Bakis, C. E., and Wang, K. W., "New Method of Chaining Carbon Nanofibers in Epoxy," *Nanotechnology*, 19:325606 (2008), 5 p.  
<http://dx.doi.org/10.1088/0957-4484/19/32/325606>.

Manoharan, M. P., Sharma, A., Desai, A. V., Haque, M. A., Bakis, C. E., and Wang, K. W., "The Interfacial Strength of Carbon Nanofiber Epoxy Composite using Single Fiber Pullout Experiments," *Nanotechnology*, 20:295701 (2009), 5 p.  
<http://dx.doi.org/10.1088/0957-4484/20/29/295701>.

Sharma, A., Bakis, C. E., and Wang, K. W., "Effect of Electrostatic and Electro-Hydrodynamic Forces on the Chaining of Carbon Nanofibers in Liquid Epoxy," *J. Physics D: Applied Physics*, 43:175402 (2010), 10 p. <http://dx.doi.org/10.1088/0022-3727/43/17/175402>.

Liu, A., Wang, K. W., and Bakis, C. E., "Multiscale Damping Model for Polymeric Composites Containing Carbon Nanotube Ropes," *J. Composite Materials*, 44(19): 2301-2323 (2010). <http://dx.doi.org/10.1177/0021998310365176>.

### **Conferences**

Sharma, A., Bakis, C. E., and Wang, K. W., "Electrically Aligned Carbon Nanofiber/Epoxy Composites," *Proc. 22<sup>nd</sup> Technical Conference*, American Society for Composites, DEStech Publications, Lancaster, PA, 2007. Paper No. 213, 10 p. (CD ROM).

Sharma, A., Bakis, C. E., and Wang, K.-W., "Tailored Alignment of Functionalized Multiwall Carbon Nanotubes in Epoxy," *Proc. 2008 Fall Technical Conference*, Society for the Advancement of Materials and Process Engineering, Covina, CA, 2008, ISBN 978-1-934551-04-2, Paper No. 41, 11 p. (CD-ROM).

Liu, A., Wang, K. W., and Bakis, C. E., "Multiscale Analysis of the Effect of Carbon Nanotube (CNT) Functionalization on Damping Characteristics of CNT-Based Composites," *Active and Passive Smart Structures and Integrated Systems 2010*, Proc. SPIE, Vol. 7643, M. N. Ghasemi-Nejhad, Ed., SPIE - The International Society for Optical Engineering, Bellingham WA, 2010, <http://dx.doi.org/10.1117/12.847250>, 9 p.

Liu, A., Wang, K. W., and Bakis, C. E., "Damping Characteristics of Carbon Nanotube-Epoxy Composites via Multiscale Analysis," *Proc. 51<sup>st</sup> AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conf.*, American Inst. of Aeronautics and Astronautics, Reston, VA, 2010, Paper No. 2010-2896, 8 p. (CD ROM).

Liu, A., Wang, K. W., and Bakis, C. E., "Damage Detection of Epoxy Polymer via Carbon Nanotube Fillers and External Circuitry," *World J. Engineering*, Vol. 7, Supplement 2, Sept. 2010, Proc. Intl. Conf. on Composites/Nano Engineering, ICCE-18, paper 358, 2 p.

## **VII. Awards and Honors, 2007-10**

C. E. Bakis

- University Distinguished Professor, Penn State University, Dec. 2007
- Fellow of the International Institute for Fiber Reinforced Polymers in Construction (IIFC), 2008
- Award of Appreciation, American Society for Testing and Materials, Committee D30 on Composite Materials

- Best Paper Award in Structural Dynamics and Control, Adaptive Structures and Material Systems Committee, Aerospace Division, American Society of Mechanical Engineers, 2010
- Outstanding Research Award, Penn State Engineering Alumni Society, 2010.
- Fellow, American Society for Composites, 2010.
- Recording Secretary of the American Society for Composites for 2010 and 2011

K.W. Wang

- N. O. Myklestad Award, American Society of Mechanical Engineers, 2007
- Stephen P. Timoshenko Collegiate Chair of Mechanical Engineering, University of Michigan, 2008
- Adaptive Structures and Material Systems Prize, American Society of Mechanical Engineers, 2008
- NASA Tech Brief Award, 2008
- Wei Lun Distinguished Visiting Professorship, Chinese Univ. of Hong Kong, 2008
- Distinguished Visiting Professorship, Feng Chia University, Taiwan, 2008-2009
- Rudolf Kalman Best Paper Award, American Society of Mechanical Engineers, 2009
- Fellow of the Institute of Physics (IOP), 2010
- Associate Fellow of the American Institute of Aeronautics and Astronautics, 2010
- Best Paper Award in Structural Dynamics and Control, Adaptive Structures and Material Systems Committee, Aerospace Division, American Society of Mechanical Engineers, 2010

### **VIII. Graduate Students Involved Directly in ARO Project**

Ailin Liu, PhD, Mechanical and Nuclear Engineering Dept., Penn State University. Dr. Liu successfully defended her dissertation on 17 Aug 2009.

Ambuj Sharma, PhD, Engineering Science and Mechanics Dept., Penn State University. Dr. Sharma successfully defended his dissertation on 12 July 2010.

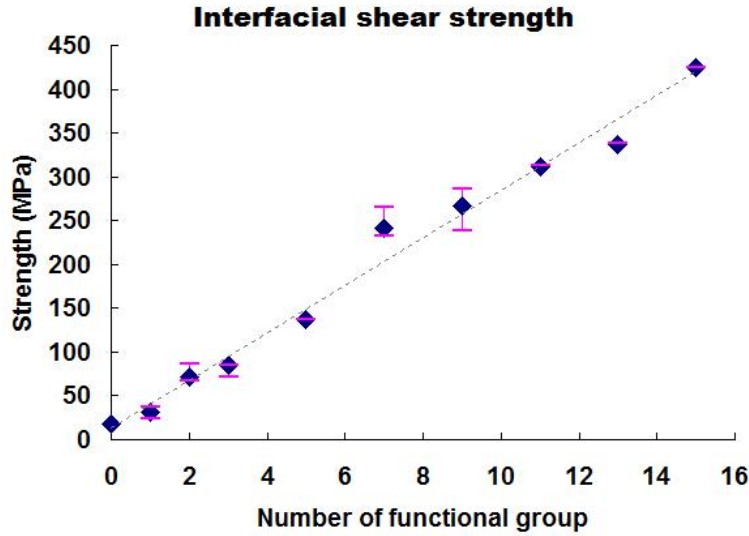


Figure 1. SWNT/epoxy interfacial shear strength for different numbers of functional groups at the interface. Each SWNT contains 1000 atoms.

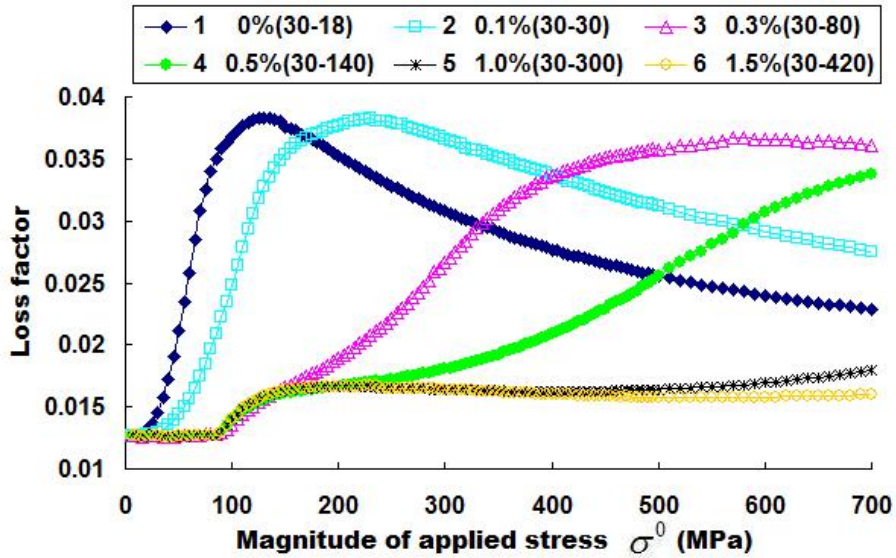


Figure 2. Loss factor of epoxy composite with in-plane randomly-oriented functionalized SWNT ropes under tension-compression cyclic loading. The legend indicates the case number, the CNT functionalization scale, and the corresponding two interfacial shear strengths at the inter-tube and CNT/epoxy interface. For instance, 1 0% (30-18) represents Case 1 for a composite with non-functionalized CNTs, which has inter-tube shear strength of 30 MPa and CNT/epoxy shear strength of 18 MPa.



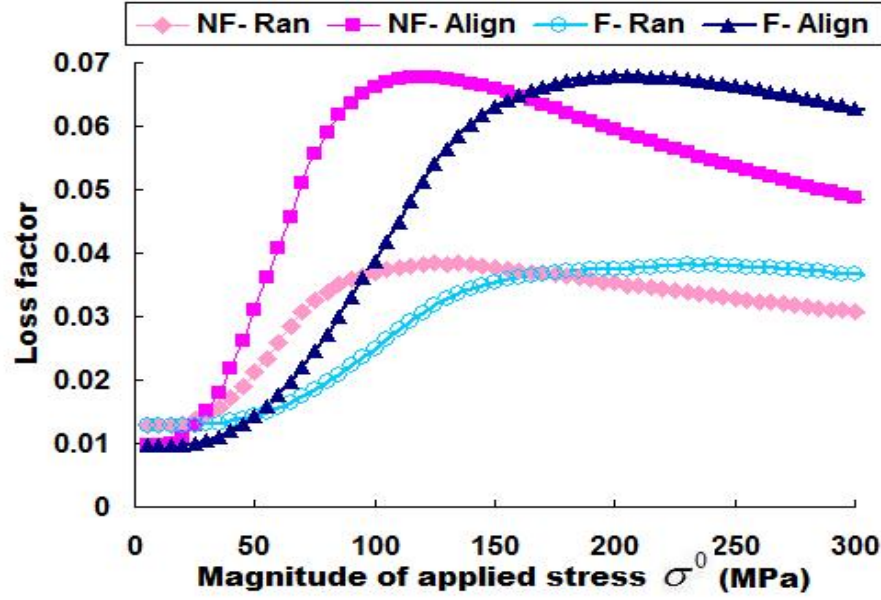


Figure 3. Loss factor of composites with 0° aligned and in-plane randomly oriented nanoropes under fully-reversed tension-compression loading. NF represents composite with non-functionalized SWNT ropes; F indicates composite containing SWNT ropes with 0.1% functionalization.

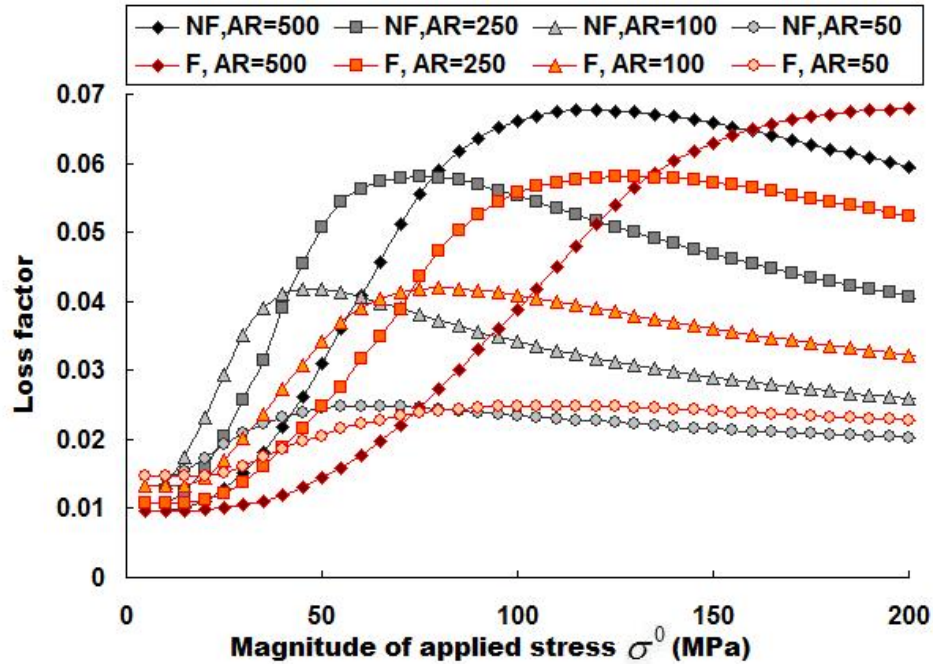


Figure 4. Effect of CNT aspect ratio on damping in composites with 0° aligned nanoropes under fully-reversed tension-compression loading. NF represents composite with non-functionalized SWNT ropes; F indicates composite containing SWNT ropes with 0.1% functionalization.

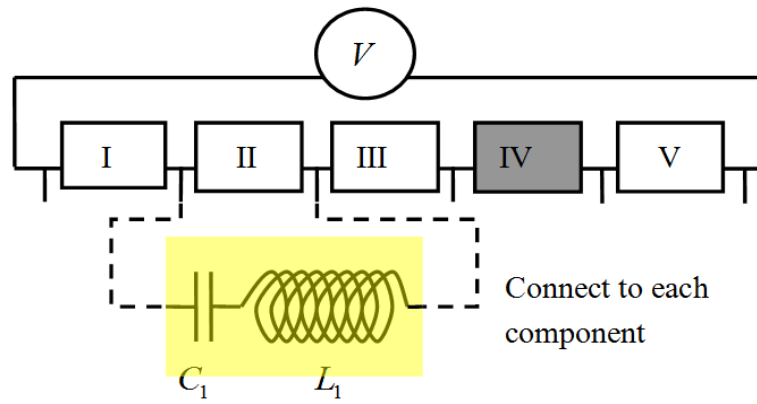


Figure 5. Illustration of resistor chain with five components. Section IV is damaged.

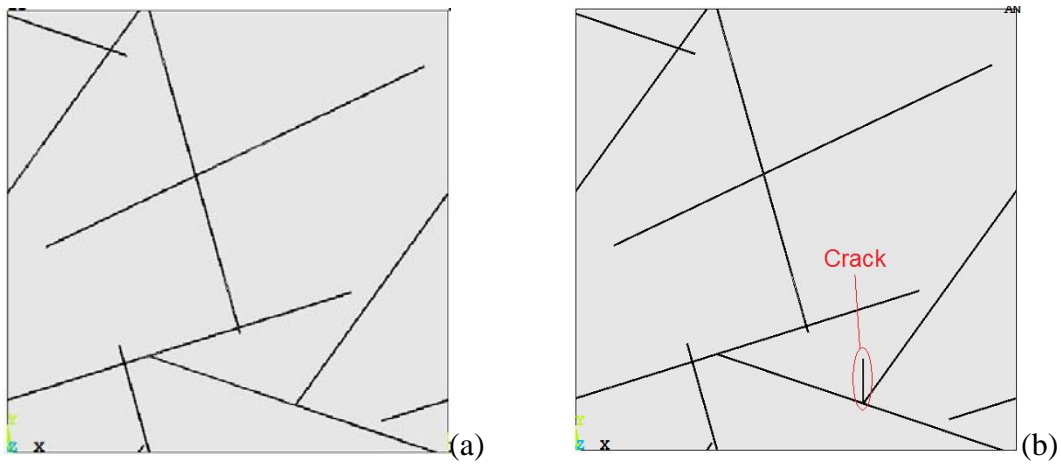


Figure 6. 2D FE model of composite layer: (a) healthy structure, (b) damaged with a crack

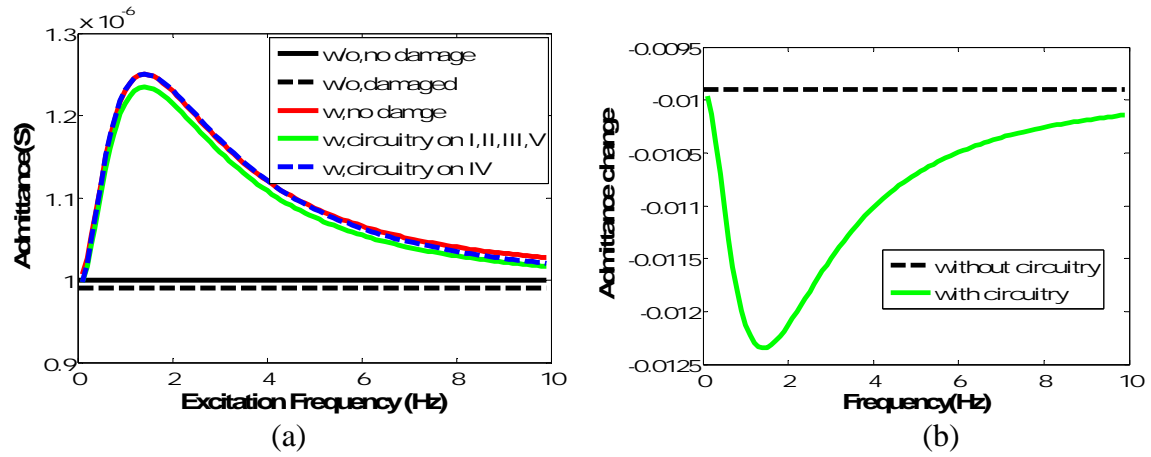


Figure 7. Electric admittance (a) and admittance change (b) for 1D resistor chain model. Here ‘w/o’ represents without circuitry and ‘w’ means with circuitry.  $L_1=50$  kH,  $C_1=0.01$  mF.

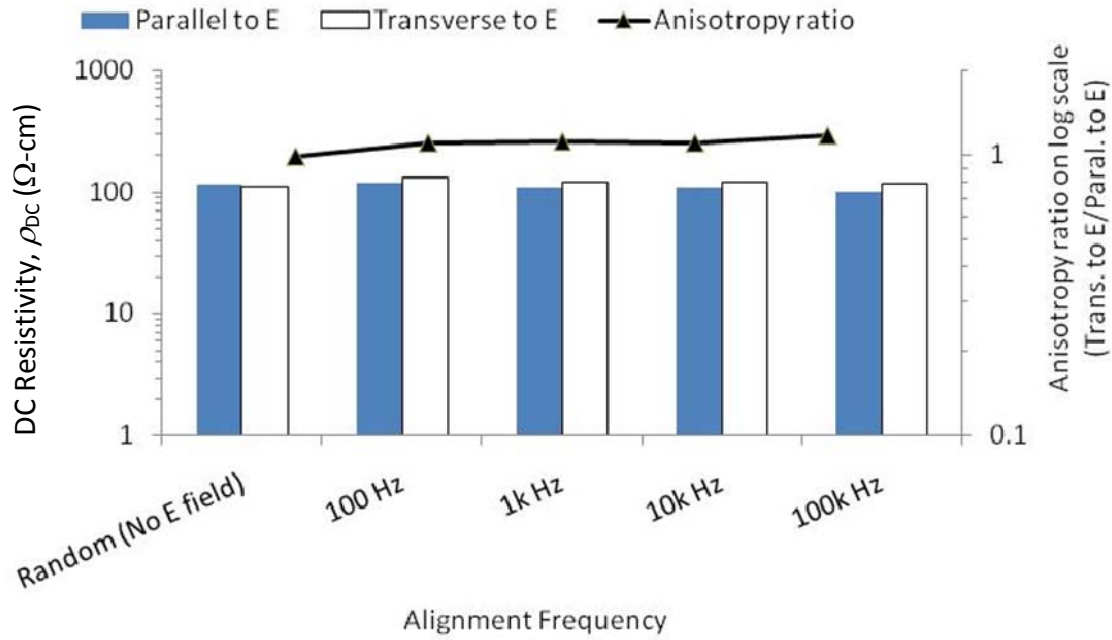


Figure 8. DC resistivity of unfunctionalized MWCNT specimens prepared with various frequencies.

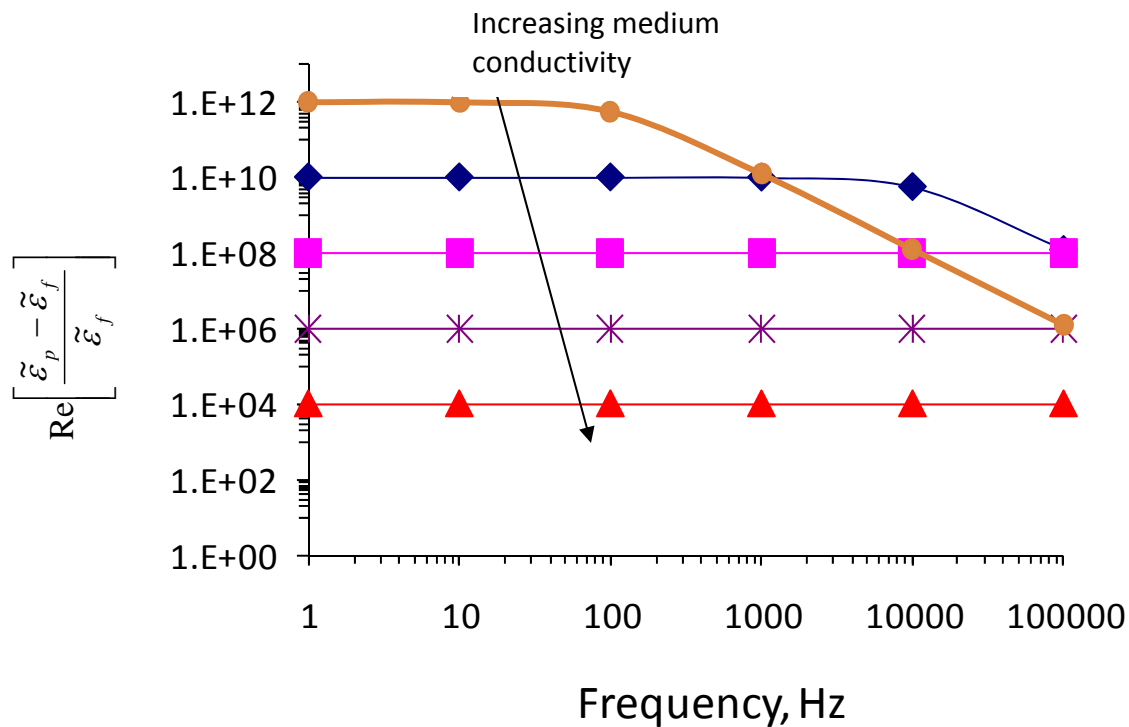


Figure 9. Variation of the CM factor with frequency and medium conductivity.

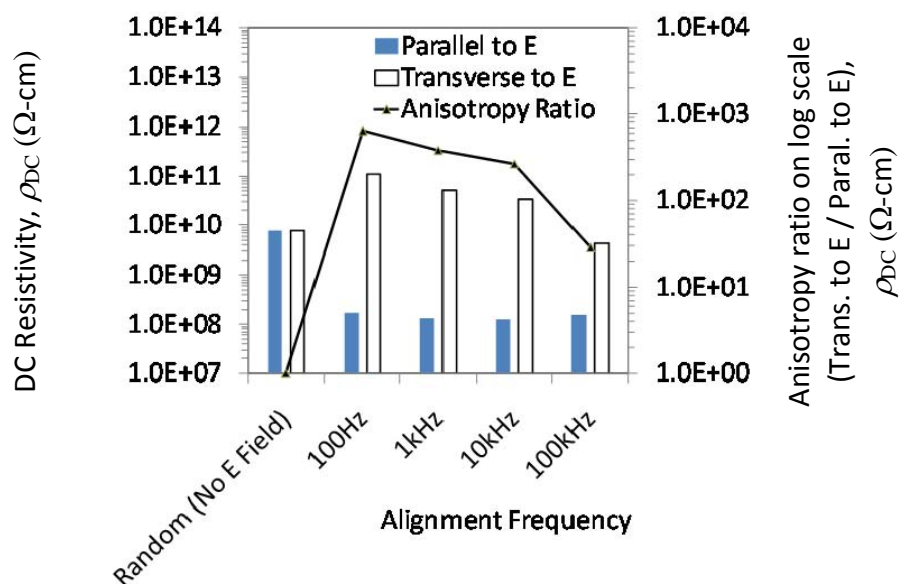


Figure 10. DC resistivity of non-covalently functionalized MWCNT specimens prepared with various frequencies

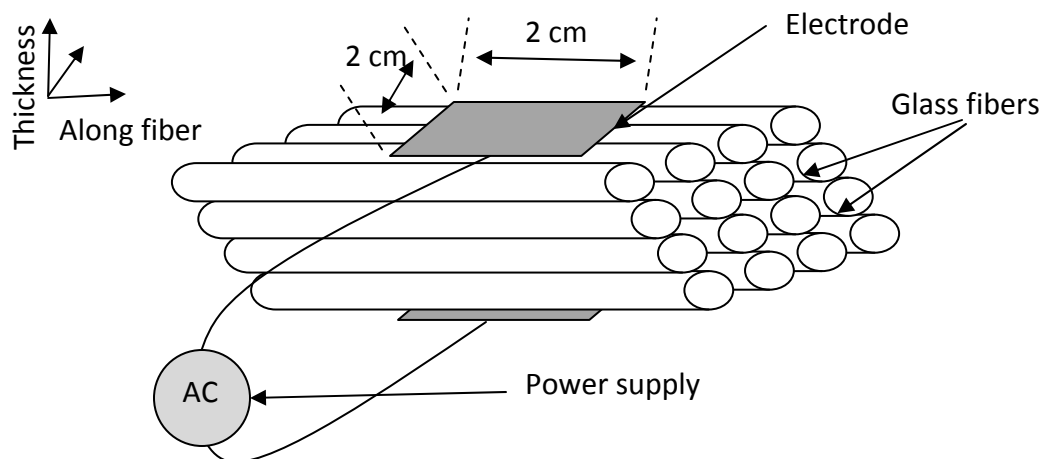


Figure 11. Schematic of experimental setup used for aligning CNTs in glass-fiber composites.

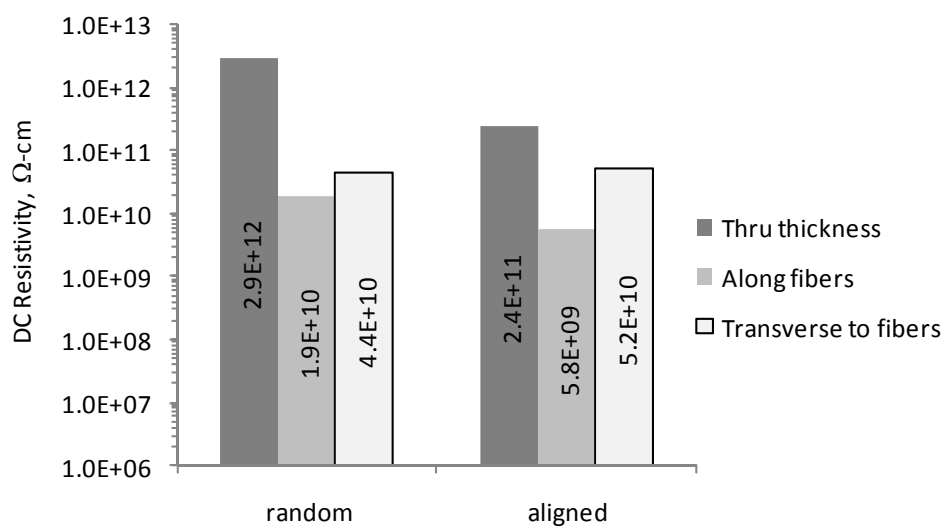


Figure 12. DC resistivity of non-covalently functionalized MWCNT/continuous glass fiber/epoxy composite manufactured with glass fiber volume fraction of 0.45 (orifice size 0.031 in.). Electric field of 1000 V/cm was applied at 1 kHz.

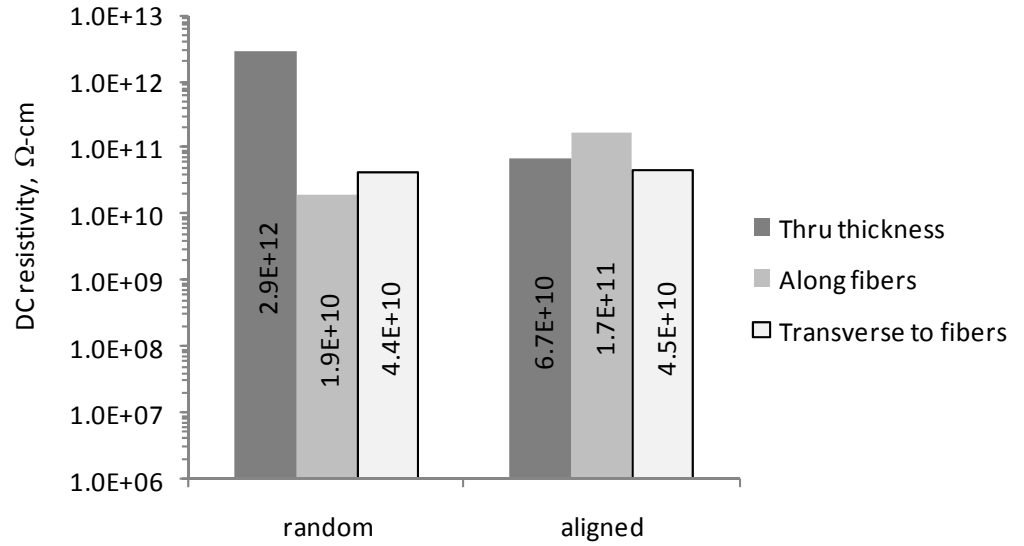


Figure 13. DC resistivity of non-covalently functionalized MWCNT/continuous glass fiber/epoxy composite manufactured with glass fiber volume fraction of 0.45 (orifice size 0.031 in.). Electric field of 1000 V/cm was applied at 100 Hz.

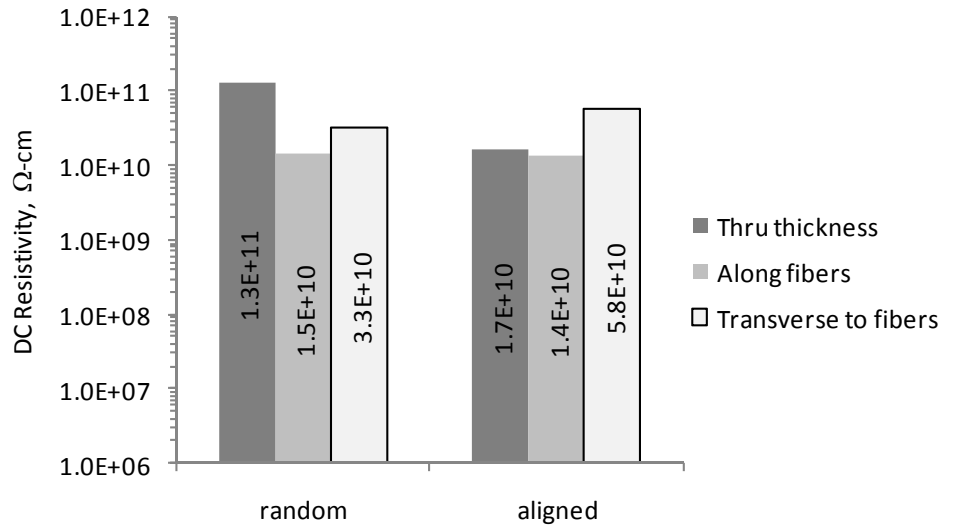


Figure 14. DC resistivity of non-covalently functionalized MWCNT/continuous glass fiber/epoxy composite manufactured with glass fiber volume fraction of 0.55 (orifice size 0.038 in.). Electric field of 1000 V/cm was applied at 1 kHz.

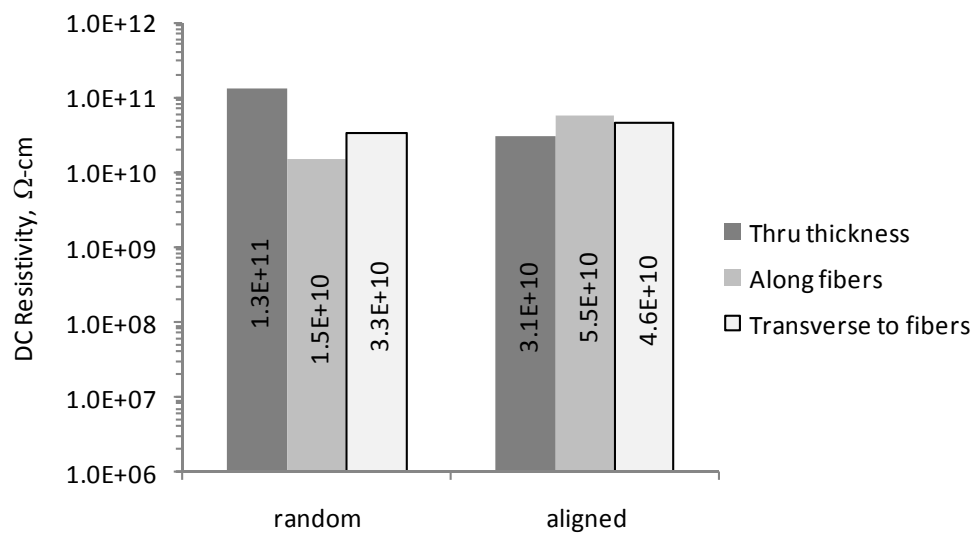


Figure 15. DC resistivity of non-covalently functionalized MWCNT/continuous glass fiber/epoxy composite manufactured with glass fiber volume fraction of 0.55 (orifice size 0.038 in.). Electric field of 1000 V/cm was applied at 100 Hz.